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COMPARISON BETWEEN MEASURED CONCENTRATIONS OF PHOTOOXIDANTS (H$_2$O$_2$, O$_3$) IN AIR AND RESULTS OBTAINED FROM SIMPLE CHEMICAL KINETIC MECHANISM

Field data on the temporal evolution of hydrogen peroxide and ozone concentrations in air coming from urban (51°07' N, 17°02' E, 116 m a.s.l.) and mountainous (50°79' N, 15°51' E, 1362 m a.s.l.) areas were compared to simple model results based on OH–HO$_2$–NO$_x$–CO–HCHO–O$_3$ and NO$_x$–O$_3$ chemical kinetics. For some chosen days the model described quite satisfactorily the photochemical processes influencing the concentrations of oxidants both in urban and mountainous air.

1. INTRODUCTION

Ozone and hydrogen peroxide have been found both in unpolluted and polluted atmosphere. As active oxidants they react rapidly in the troposphere principally with sulfur dioxide in cloud or rain droplets. H$_2$O$_2$ also plays an important role in the balance of free radicals by acting as a reservoir of hydroperoxy radicals [1], [2] and O$_3$ can react with organic compounds [3]–[6]. Therefore, it is very important to forecast theirs concentrations in ambient air, particularly O$_3$ and H$_2$O$_2$ can be considered as indicators of a photochemical smog.

The purpose of the present work was to compare "typical" daily maximum concentrations of hydrogen peroxide and ozone registered in an urban air and in the mountains with model predictions using a simple approach based on the OH–HO$_2$–NO$_x$–CO–HCHO–O$_3$ and NO$_x$–O$_3$ chemical kinetics.

2. EXPERIMENTAL

Measurements of 30-min averaged gaseous phase hydrogen peroxide and ozone concentrations together with some air pollutants (NO$_x$, CO, SO$_2$ and BTX) and meteoro-

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logical parameters (temperature, humidity, solar radiation, wind speed and direction) were performed in the Wrocław University of Technology Air Quality Monitoring Station (51°07' N, 17°02' E, 116 m a.s.l.) located close to the main road in the city and in the Sudeten Mountains, the south-western Poland, at Szrenica Mount (50°79' N, 15°51' E, 1362 m a.s.l.). The localization of sampling sites is shown in figure 1.
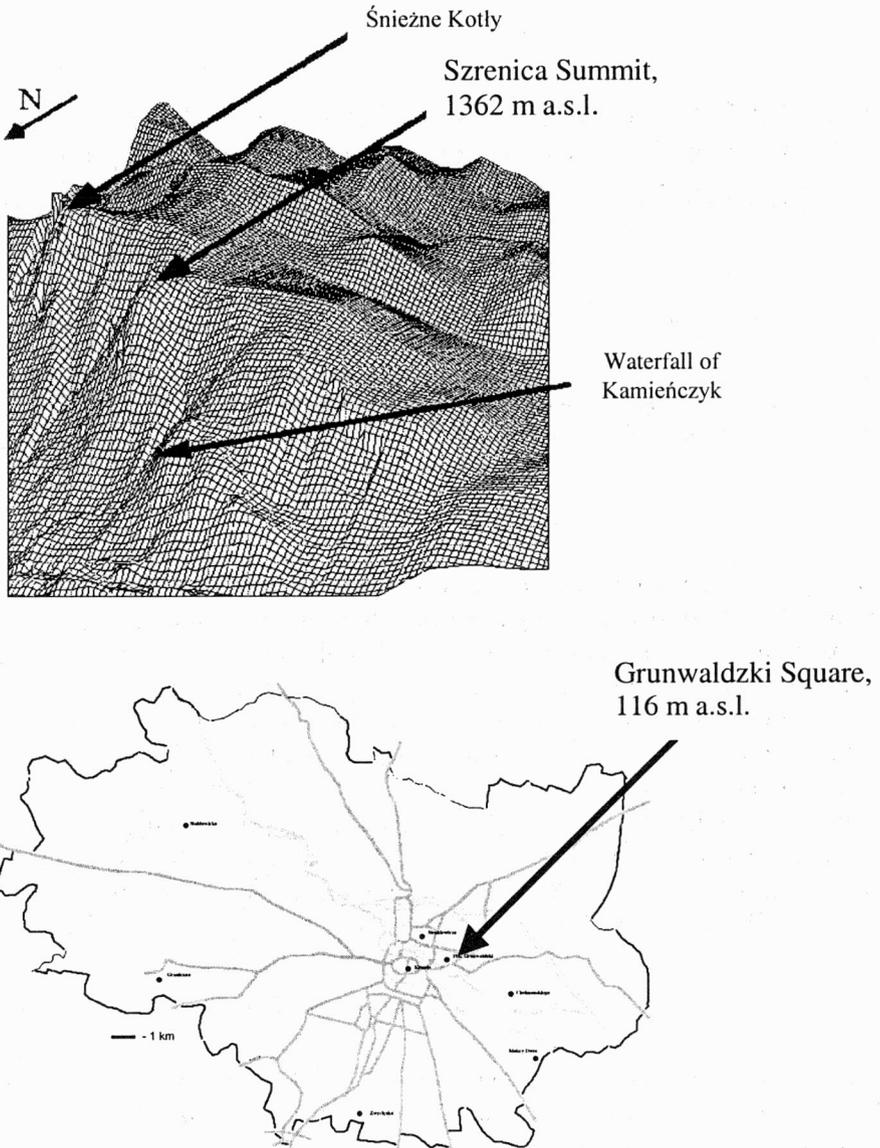

Fig. 1. Location of sampling points

Field measurements were carried out during different periods from 1996 to 2001. This paper reports data from three summertime campaigns in June 1998, August 2000 (urban atmosphere) and July 1999 (mountainous atmosphere), each of about 2–3 weeks.

The concentration of hydrogen peroxide was measured by an automatic chemiluminescence analyzer according to the method provided and described by KOK et al. [7] and AMES et al. [8]. Ozone, nitrogen oxides and carbon monoxide automatic HORIBA analyzers (APOA-360, APNA-350E, APMA-350E) were operated on the principle of UV absorption, chemiluminescence and IR absorption, respectively. Meteorological data (wind speed and direction, temperature, relative humidity, pressure and radiation) were available from the automatic weather station (Campbell Scientific Ltd. ser. no. 2192) installed near the sampling points.

3. MODEL

The box model governing equation is simplified and restricted to the gaseous phase chemistry and deposition. Thus the rate of change of the hydrogen peroxide and ozone concentrations can be expressed as:

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = C - \frac{v_d}{H}[\text{H}_2\text{O}_2],$$

$$\frac{d[\text{O}_3]}{dt} = C - \frac{v_d}{H}[\text{O}_3],$$

where C is a term representative of the gaseous phase photooxidants chemistry (production and destruction), v_d is the dry deposition velocity and H is the height of the boundary layer.

The gaseous phase chemistry of hydrogen peroxide and ozone is based on the OH–HO$_2$–NO$_x$–CO–HCHO–O$_3$ and NO$_x$–O$_3$ chemical kinetics and is represented by 8 and 3 reactions, respectively. These reactions and rate constants are given in the table. Both in the H$_2$O$_2$ and O$_3$ models, it was assumed steady state for excited oxygen and oxygen atoms. Nitric oxides, carbon monoxide and ozone (in the case of hydrogen peroxide simple model) concentrations as well as solar radiation are available from on-site observations. The formaldehyde concentration is selected according to the data of BOWMAN and SEINFELD [9].

Table

Chemical reactions of importance in production and destruction
of gaseous H_2O_2 and O_3 in the troposphere

H_2O_2 chemistry	
Reaction	Rate constant
$CO + OH^{\bullet} \xrightarrow{O_2} HO_2^{\bullet} + CO_2$	$k_1 = 2.2 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1}
$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$	$k_2 = 5.6 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}
$H_2O_2 + OH^{\bullet} \longrightarrow HO_2^{\bullet} + H_2O$	$k_3 = 1.69 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}
$HO_2^{\bullet} + NO \longrightarrow NO_2 + OH^{\bullet}$	$k_4 = 8.5 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}
$H_2O_2 + hv \longrightarrow OH^{\bullet} + OH^{\bullet}$	$j_5 = j_{n5} \cdot I_n(t)$,
	where $j_{n5} = 1.21 \cdot 10^{-6} \div 1.35 \cdot 10^{-7}$ s^{-1},
	$I_n(t)$ – normalised curve of solar irradiation in function of time
$HCHO + hv \xrightarrow{2O_2} 2HO_2^{\bullet} + CO$	$j_6 = j_{9p} \cdot I_n(t)$,
	where $j_{9p} = 3.55 \cdot 10^{-5} \div 6.53 \cdot 10^{-7}$ s^{-1},
$O_3 + hv \longrightarrow (O^1D) + O_2$	$j_7 = j_{7p} \cdot I_n(t)$,
	where $j_{7p} = 4.32 \cdot 10^{-5} \div 7.82 \cdot 10^{-8}$ s^{-1},
$(O^1D) + H_2O \longrightarrow 2OH^{\bullet}$	$k_8 = 2.2 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1}
O_3 chemistry	
$NO_2 + hv \longrightarrow NO + O$	$j_1 = j_{n1} \cdot I_n(t)$,
	where $j_{n1} = 9.49 \cdot 10^{-3} \div 7.32 \cdot 10^{-4}$ s^{-1},
$O + O_2 + M \longrightarrow O_3 + M$	$k_2 = 6 \cdot 10^{-34}$ cm^6 molecule^{-2} s^{-1}
$O_3 + NO \longrightarrow NO_2 + O_2$	$k_3 = 1.8 \cdot 10^{-14}$ cm^3 molecule^{-1} s^{-1}

4. RESULTS AND DISCUSSION

The comparison between hydrogen peroxide and ozone field data and model pre-
dictions for both urban and mountainous atmosphere was made for the days with the
"typical" daily maximum in theirs concentrations at midday and early afternoon
hours. The results are presented in figures 2 and 3.

Similar diurnal patterns with daytime maxima and nighttime minima were ob-
served both in the simulation and measurements. However, when the increasing role
of advection processes and the inflow of air masses from other areas were registered,
important discrepancies between measured and modelled values of ozone concentra-
tions in urban air were found. In the case of mountainous atmosphere, the concentra-
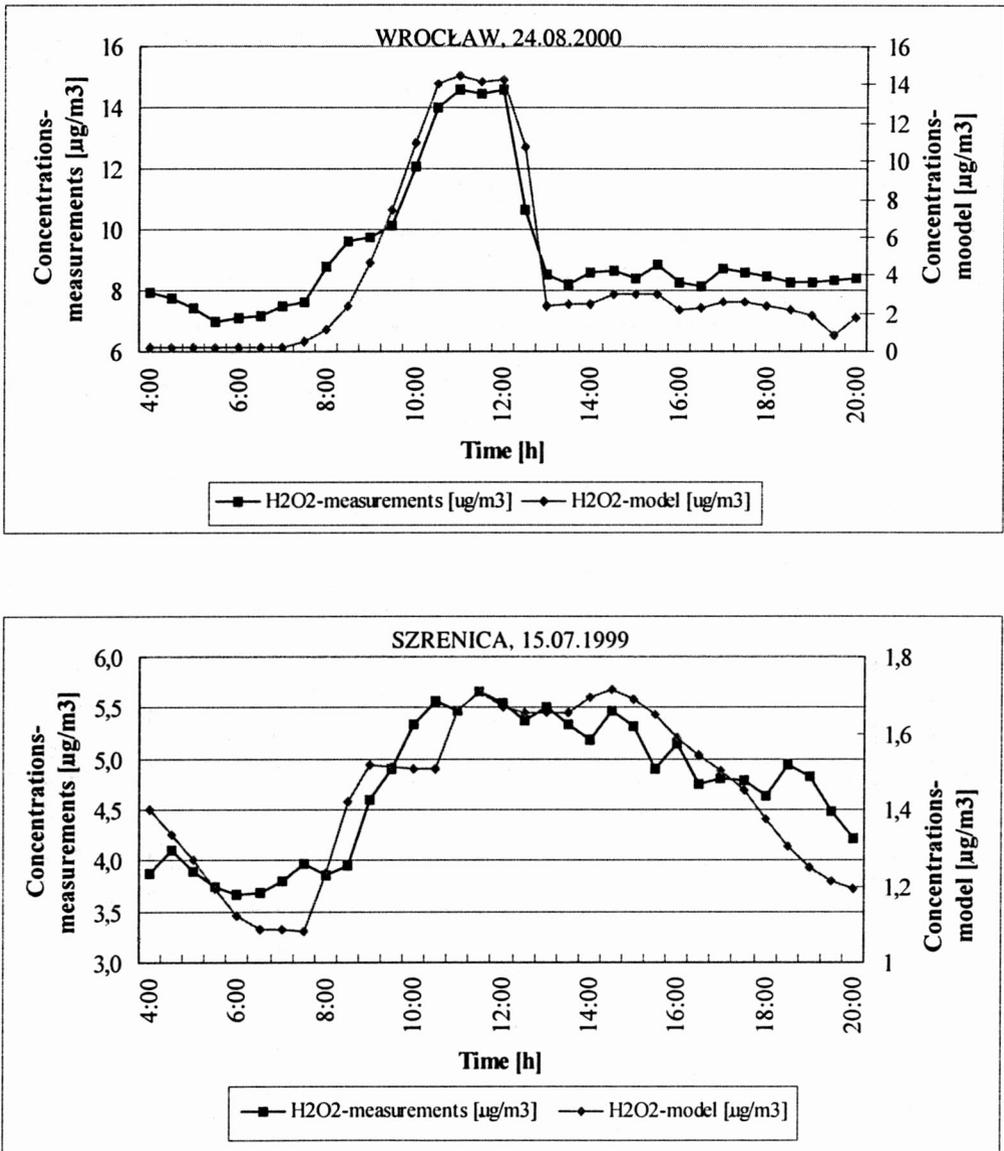
Fig. 2. Comparison between H_2O_2 concentrations modelled and measured

tion was significantly less in the simulation than in the measurements. These discrepancies may arise from many reasons, e.g. some important processes which govern the levels of oxidant substances were not included (e.g. BVOC photochemistry) in the model or there were some uncertainties associated with the formaldehyde input data of the model.
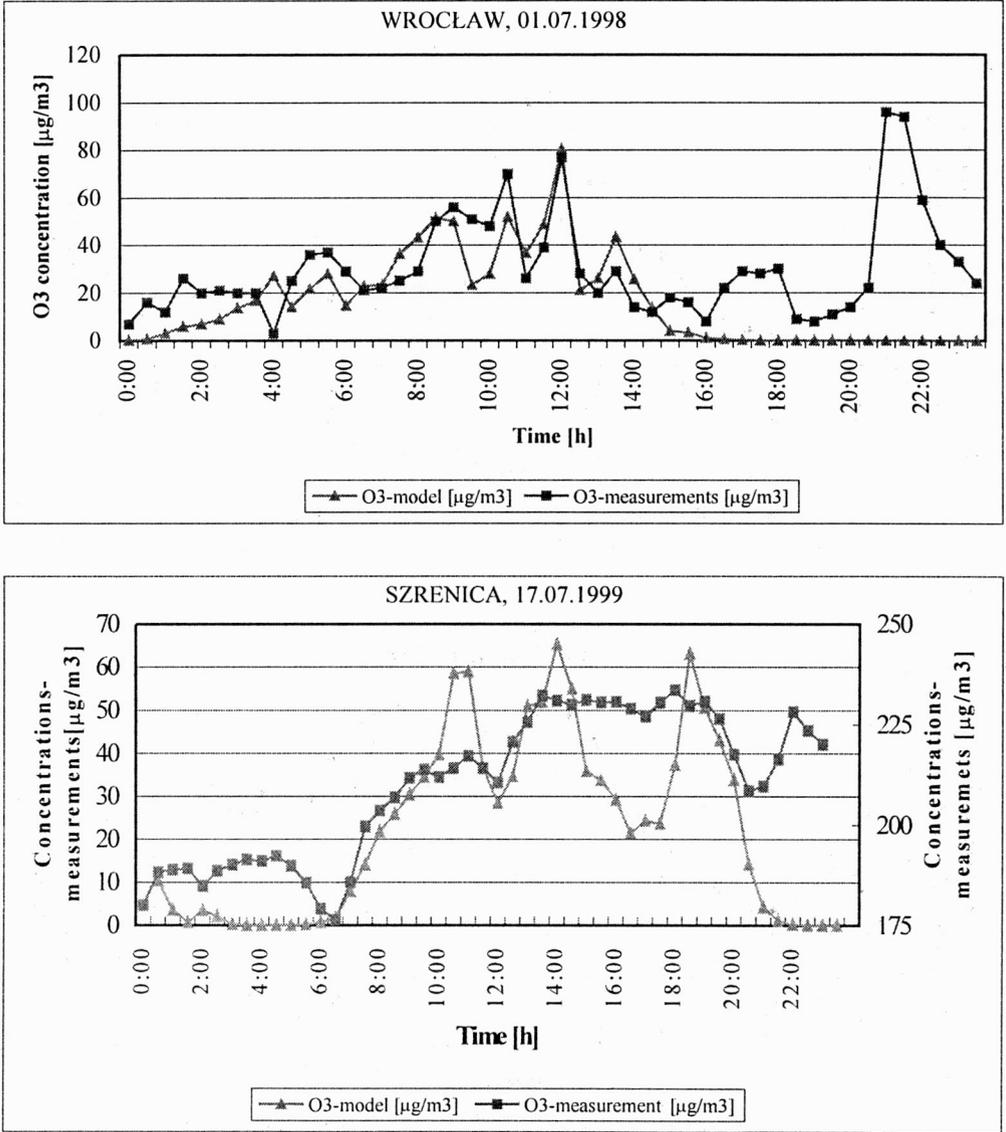
Fig. 3. Comparison between O_3 concentrations modelled and measured

Because a satisfactory model performance (in the case of H_2O_2) was obtained for the urban air, we decided to assess the sensitivity of model output to formaldehyde concentrations for the mountainous site. Results for four simulations are presented in figure 4. The data indicates that a distinct increase in H_2O_2 concentrations due to an increase in formaldehyde concentrations occurs. The simulation presented in figure 4
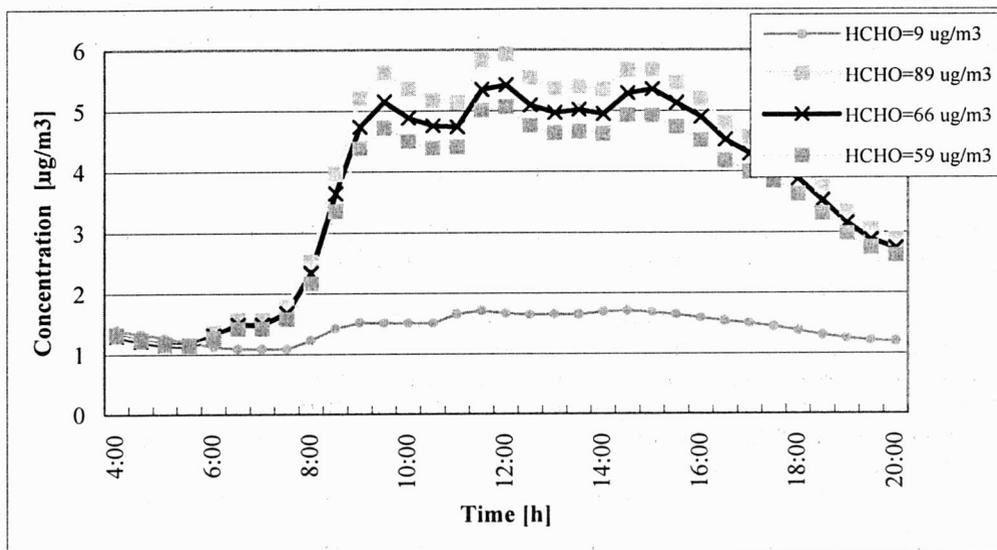
Fig. 4. Predicted H_2O_2 concentrations for different formaldehyde input data

shows that there is reasonable agreement between the measured and calculated H_2O_2 concentrations as formaldehyde concentration equal to 66 $\mu g/m^3$. It is likely that formaldehyde concentration is generally higher than the value assumed in the model (9 $\mu g/m^3$) as the region under study is considered as pollutant-impacted industrial area.

5. CONCLUSIONS

A simple approach based on the $OH–HO_2–NO_x–CO–HCHO–O_3$ and $NO_x–O_3$ chemical kinetics described quite satisfactorily the photochemical processes influencing oxidant concentrations both in the urban and mountainous air. Modelling studies confirmed that main parameters influencing ozone formation and destruction processes during daytime were solar radiation and nitrogen oxides' concentrations. In the case of hydrogen peroxide, solar radiation and concentrations of carbon monoxide, ozone, nitrogen oxide and formaldehyde affected these processes.

Important discrepancies between measured and modelled values were observed for night hours when the inflow of air masses from other areas was registered.

In terms of mountainous atmosphere, the model results showed a serious underestimation in the concentrations of oxidants in comparison to measurements. However, the sensitivity study of the H_2O_2 model output to formaldehyde concentrations has revealed that there is reasonable agreement between the measured and calculated

H_2O_2 for higher formaldehyde concentration than that assumed in the model. Further studies are necessary to test this method with formaldehyde data from a variety of field measurements.

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PORÓWNANIE ZMIERZONYCH STĘŻEŃ FOTOUTLENIACZY (H_2O_2, O_3) W POWIETRZU Z WARTOŚCIAMI UZYSKANYMI Z PROSTEGO MODELU KINETYCZNEGO

Porównano wyniki czasowego rozkładu stężeń nadtlenku wodoru i ozonu, zmierzonych w atmosferze miejskiej ($51^\circ07'$ N, $17^\circ02'$ E, 116 m n.p.m.) i górskiej ($50^\circ79'$ N, $15^\circ51'$ E, 1362 m n.p.m.) z wartościami uzyskanymi z prostego modelu kinetycznego opartego na schemacie $OH-HO_2-NO_x-CO-HCHO-O_3$ i NO_x-O_3. Dla wybranych dni wykorzystany mechanizm chemiczny zadowalająco odzwierciedlił zmiany stężeń zarejestrowane w powietrzu na obszarze miejskim i górskim.